



## A thermodynamic modelling study of aqueous tetra-n-butyl ammonium halide solutions

Sun, Li; Liang, Jierong

*Published in:*  
International Journal of Electrochemical Science

*Link to article, DOI:*  
[10.20964/2020.10.39](https://doi.org/10.20964/2020.10.39)

*Publication date:*  
2020

*Document Version*  
Publisher's PDF, also known as Version of record

[Link back to DTU Orbit](#)

*Citation (APA):*  
Sun, L., & Liang, J. (2020). A thermodynamic modelling study of aqueous tetra-n-butyl ammonium halide solutions. *International Journal of Electrochemical Science*, 15, 9902-9916. <https://doi.org/10.20964/2020.10.39>

---

### General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

# A Thermodynamic Modelling Study of Aqueous Tetra-n-butyl Ammonium Halide Solutions

Li Sun<sup>1,2,\*</sup>, Jierong Liang<sup>3</sup>

<sup>1</sup> Department of Chemical and Biochemical Engineering, Technical University of Denmark, 2800, Kgs. Lyngby, Denmark

<sup>2</sup> College of Mechanical and Electrical Engineering, Hohai University, Changzhou 213022, People's Republic of China

<sup>3</sup> Department of Energy Conversion and Storage, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark

\*E-mail: [lsun@kt.dtu.dk](mailto:lsun@kt.dtu.dk)

*Received:* 10 June 2020 / *Accepted:* 7 August 2020 / *Published:* 31 August 2020

---

This work presents a novel model for aqueous electrolyte solutions that extends the Cubic Plus Association Equation of State by combining the Debye–Hückel theory for electrostatic interactions. This model is applied to perform a fluid phase modelling study of aqueous tetra-n-butyl ammonium halide solutions. The interaction parameters between cations/anions and water are evaluated by regression of the experimental mean ionic activity coefficients (MIAC) of the electrolyte. The results show that this novel model correlates reasonably well with the experimental MIAC (for example, the relative average deviations are 6.3% for the MIAC of tetra-n-butyl-ammonium bromide). The interaction parameters between cations/anions and gas are evaluated by regression of the experimental gas solubilities. The results show that this novel electrolyte model correlates reasonably well with gas solubility (for example, the relative average deviations are 2.9% for the nitrogen solubility in aqueous tetra-n-butyl-ammonium bromide solutions). For a more complete evaluation of the model, the electrostatic terms, parameter estimation approaches, and salting effects on gas solubility are analysed and discussed in detail.

---

**Keywords:** Aqueous Tetra-n-butyl Ammonium Halide Solutions; Electrolyte Equation of State; Debye–Hückel Theory; Hydrophobic Effect

## 1. INTRODUCTION

Special kinds of hydrates can be formed in the presence of certain additives (e.g., some quaternary ammonium salts). These formed hydrates are called semi-clathrate hydrates (SCH). The structures of SCH are more stable than those of normal hydrates.

In SCH, water (H<sub>2</sub>O) molecules and the cations of additives are combined to build a clathrate, with the cations embedded in the framework cavities, while small guest gas (e.g., nitrogen (N<sub>2</sub>), carbon dioxide (CO<sub>2</sub>) and methane (CH<sub>4</sub>)) molecules can be captured in small empty cages [1, 2].

Since SCH are stable even at atmospheric pressure, SCH attract attention because of their promising applications, including thermal storage, gas sequestration, and gas transportation [3, 4].

Pressure, temperature, and electrolyte molality determine the phase equilibrium conditions of SCH systems; phase modelling of SCH systems is developed by equating the fugacity of H<sub>2</sub>O in the hydrate phase and the aqueous phase [5, 6]. Therefore, fluid-phase modelling is a critical part of hydrate-liquid-gas modelling. Thermodynamic models of electrolyte solutions have been developed by combining long-range electrostatic interactions with a model (i.e., Equations of State (EoS)) of short-range forces.

As the most common additives used to form SCH, tetra-*n*-butyl ammonium halides (TBAX) receive most attention [1-4, 7]. The models presented for TBAX fluid systems can be divided into two different approaches.

The  $\phi$ - $\gamma$  approach is the more common approach: among these models, the electrolyte Non-Random Two Liquid (e-NRTL) model [8] is the most used activity coefficient model.

In combination with e-NRTL, several models have been presented based on the Soave-Redlich-Kwong EoS (SRK) [9, 10], the Trebble–Bishnoi EoS (TB) [11, 12], and the Peng-Robinson EoS (PR) [13, 14]. Najibi and co-workers [15] combined the PR EoS [14] with “Mean Spherical Approximation including ionic hydration and association” [16] for aqueous solutions of tetra-*n*-butyl ammonium bromide (TBAB).

Contrasting the  $\phi$ - $\gamma$  models, the  $\phi$ - $\phi$  approach uses an electrolyte EoS (e-EoS) to describe both the vapour and liquid phases. Relatively few e-EoS studies have been presented to date for TBAX systems. To the best of our knowledge, only three  $\phi$ - $\phi$  models have been applied for TBAX fluid systems: “statistical associating fluid theory for potentials of variable range for electrolyte solutions” (SAFT-VRE) [17], modified Patel-Teja EoS (MPT) [18] and electrolyte Cubic Plus Association EoS (e-CPA) [19]. Paricaud [17] used SAFT-VRE to model TBAB fluid systems, and then, Fukumoto et al. [20] and Babu et al. [21] made improvements of SAFT-VRE and modelled some TBAX systems. In SAFT-VRE models, the interaction parameters between salt and H<sub>2</sub>O are evaluated by the regression of the mean ionic activity coefficients (MIAC) of TBAX. Gas solubility is calculated from vapour-liquid flash calculations, and it should be noted that the effects of TBAB on the gas phase are negligible in their works [17, 20]. Ma et al. [22] applied MPT [18] to model aqueous solutions of TBAB and tetra-*n*-butyl ammonium fluoride (TBAF). In their modelling [22], the salt-H<sub>2</sub>O interaction parameters and salt-gas interaction parameters were evaluated by the regression of MIAC and gas solubility in aqueous TBAB solutions, respectively. Sun et al. [23] modelled several TBAX fluid systems by using e-CPA [19]. In their works [23], the ions-H<sub>2</sub>O and ions-gas interaction parameters were evaluated from the regression of MIAC and gas solubility in aqueous TABX solutions, respectively. Gas solubility is calculated using the vapour-liquid flash calculation in the work of Sun et al. [23], which is also extensively discussed the salting effects of TBAX.

To date, fluid phase modelling of H<sub>2</sub>O+gas+TBAX systems has not been systematically studied, and limited e-EoS have been presented for such systems.

It is of interest to develop an e-EoS that is easy to use and has a relatively high modelling accuracy for TBAX systems. In this work, a novel e-EoS based on CPA [24] is presented for modelling aqueous TBAX solutions.

This contribution is divided into four parts: Section 2 presents the details of the novel e-EoS; Section 3 presents the parameter estimation; Section 4 presents the modelling results for both the binary and ternary systems; and Section 5 presents conclusions.

## 2. THERMODYNAMIC MODEL

An essential advantage of e-EoS is that it provides a consistent thermodynamic framework [25]. In this work, we try to develop an easy-to-use e-EoS that is suitable for industrial applications.

Hydrogen bonds form in liquid H<sub>2</sub>O [26], and the CPA EoS [24] was presented as suitable for describing associating fluids. In CPA, the residual Helmholtz energy is from the physical term ( $A^{SRK}$ ) and the association term ( $A^{Assoc}$ ). There are five CPA pure-compound parameters: three SRK parameters and two association parameters (only for associating components). For mixtures, the classic vdw1f mixing rules are applied for the CPA co-volume parameters (*represented as b*) and the energy parameters [24].

In CPA, the residual Helmholtz energy for the physical term (the SRK EoS) [10] is calculated from:

$$A^{SRK} = nRT \left[ -\ln \left( 1 - \frac{b}{v} \right) - \frac{a(T)}{bRT} \ln \left( 1 + \frac{b}{v} \right) \right] \quad (1)$$

where  $T$  is the temperature,  $R$  is the ideal gas constant,  $v$  is the molar volume,  $n$  is the number of moles present, and  $a(T)$  is the temperature-dependent energy parameter of the mixture.  $b$  is calculated by:

$$b = \sum_i x_i b_i \quad (2)$$

where  $x_i$  is the mole fraction of component  $i$  (solvent, gas, ion) and  $b_i$  is the pure CPA co-volume parameter.

For a binary system without electrolyte, the classical vdw1f mixing rules are used for  $a(T)$ .

$$a(T) = \sum_i \sum_j x_i x_j \sqrt{a_i(T) a_j(T)} (1 - k_{ij}) \quad (3)$$

The energy parameter of the mixture,  $a_i(T)$  is given by:

$$a_i = a_{0i} \left( 1 + c_{1i} (1 - \sqrt{T_{ri}}) \right)^2 \quad (4)$$

where  $T_{ci}$  is the critical temperature for component  $i$  and  $T_{ri}$  is the reduced temperature of component  $i$ , defined as  $T_{ri} = T/T_{ci}$ .

The association term  $A^{Assoc}$  is from Wertheim's association theory [27]:

$$A^{Assoc} = RT \left[ \sum_i n_i \sum_{A_i} \left( \ln X_{A_i} - \frac{1}{2} X_{A_i} + \frac{1}{2} \right) \right] \quad (5)$$

$$\frac{1}{X_{A_i}} = 1 + \sum_j \rho_j \sum_{B_j} X_{B_j} \Delta_{A_i B_j} \quad (6)$$

where  $n_i$  is the number of moles of component  $i$ ,  $\rho_j$  is the density of component  $j$ ,  $X_{A_i}$  is the fraction of site A of component  $i$  that is not bonded to other sites, and  $\Delta_{A_i B_j}$  is the association strength calculated by:

$$\Delta_{A_i B_j} = g(\rho) \left[ \exp\left(\frac{\varepsilon^{A_i B_j}}{k_B T}\right) - 1 \right] b_{ij} \beta^{A_i B_j} \quad (7)$$

where  $\beta^{A_i B_j}$  is the association volume,  $\varepsilon^{A_i B_j}$  is the association energy, and  $b_{ij}$  is given by  $b_{ij} = (b_i + b_j)/2$ , similar to Eq. (2). The radial distribution function is expressed as  $g(\rho) = (1 - 1.9\eta)^{-1}$ , with the packing fraction  $\eta$  defined as  $b/4v$ .

Long-range electrostatic forces between charged molecules should be considered to accurately describe the phase behaviour of systems containing electrolytes [25].

The “ion-ion+ion-H<sub>2</sub>O” (II+IW) theory [28, 29] states that the basic electrostatic interactions in electrolyte solutions are ion-ion interactions and ion-H<sub>2</sub>O interactions. Previous studies [28-30] on activity coefficients of individual ions show that both ion-ion and ion-H<sub>2</sub>O interaction combinations are equally important.

Most e-EoS [17-19, 31-33] apply Debye-Hückel theory [34] or the mean spherical approximation (MSA) [35] for ion-ion interaction calculations. Maribo-Mogensen et al. [36] studied the performances of the nonrestricted primitive MSA [35] and Debye-Hückel [34]. The investigation showed that the performance of Debye-Hückel and the MSA are similar. They also concluded that the Debye-Hückel theory is simpler than the MSA and might be able to be applied in connection with EoS without a loss of accuracy. In our model, the Debye-Hückel theory is selected for calculations of electrostatic interactions.

The Born equation [37] is used for ion-H<sub>2</sub>O interaction calculations in some thermodynamic models. However, other approaches are also presented for ion-H<sub>2</sub>O interaction calculations. Fraenkel [38] presented an extension of the Debye-Hückel theory (DH-SiS) that considers the ion and the counterion with two shells of different ion sizes. Other scholars have also presented similar treatments, and some models [33] use the hydrated ionic diameter in electrostatic interaction calculations to account for the contribution of the ion-H<sub>2</sub>O interaction.

In our model, we consider ion-H<sub>2</sub>O interactions via adjusting the ion radius in the electrostatic calculations, i.e., we use the hydrated ionic radii.

After combining the Debye-Hückel theory with the physical term and association term, a novel e-EoS is developed, and the residual Helmholtz energy is given as:

$$A^{Res} = A^{SRK} + A^{Assoc} + A^{DH} \quad (8)$$

The contribution from the ion-ion interaction  $A^{DH}$  is calculated using the Debye-Hückel theory [34]:

$$A^{DH} = -\frac{k_B T V}{4\pi N_A \sum_i n_i Z_i^2} \sum_i n_i Z_i^2 \chi_i \quad (9)$$

Here, the function  $\chi_i$  is given by:

$$\chi_i = \frac{1}{d_i^3} \left[ \ln(1 + \kappa d_i) - \kappa d_i + \frac{1}{2} (\kappa d_i)^2 \right] \quad (10)$$

where  $d_i$  is the hydrated ionic diameter of ion  $i$  and  $\kappa$  is the inverse Debye screening length given by:

$$\kappa = \left( \frac{e^2 N_A^2}{\varepsilon_r \varepsilon_0 R T V} \sum_{ions} n_i Z_i^2 \right)^{1/2} \quad (11)$$

where  $V$  is total volume in  $m^3$ ,  $N_A$  is the Avogadro constant,  $n_i$  is the number of moles of ion  $i$ , and  $Z_i$  is the charge of ion  $i$ ,  $\epsilon_0$  is the permittivity in vacuum,  $\epsilon_r$  is the relative static permittivity of the solvent.

The Huron-Vidal/NRTL mixing rule has additional flexibility to electrolyte systems [19]; for a binary system involving an ion:

$$\frac{a}{b} = \sum_i x_i \frac{a_i}{b_i} - \frac{g^{E,\infty}}{\ln 2} \quad (12)$$

$$\frac{g^{E,\infty}}{RT} = \sum_i x_i \frac{\sum_j x_j b_j \exp\left(-\alpha_{ji} \frac{\Delta U_{ji}}{RT}\right) \frac{\Delta U_{ji}}{RT}}{\sum_j x_j b_j \exp\left(-\alpha_{ji} \frac{\Delta U_{ji}}{RT}\right)} \quad (13)$$

where  $g^{E,\infty}$  is the excess Gibbs energy at infinite pressure,  $\alpha_{ji}$  is the NRTL non-randomness parameter, and  $\Delta U_{ji}$  is the change in interaction energy between like and unlike interactions.

To improve the applicability of the model, the “ion-solvent” is converted into “cation/anion-solvent” ( $\Delta U_{cation/anion-solvent}$ ), and the “ion-gas” is converted into “cation/anion-gas” ( $\Delta U_{cation/anion-gas}$ ), which means that the interaction parameter  $\Delta U_{cation-solvent}$  is equal to  $\Delta U_{anion-solvent}$  and  $\Delta U_{cation-gas}$  is equal to  $\Delta U_{anion-gas}$ .

### 3. PARAMETER ESTIMATION

In this work, three TBAX+H<sub>2</sub>O systems are studied: H<sub>2</sub>O+TBAB, H<sub>2</sub>O+tetra-n-butyl ammonium chloride (TBAC), and H<sub>2</sub>O+TBAF. Moreover, three H<sub>2</sub>O+gas+TBAX systems are studied: H<sub>2</sub>O+CO<sub>2</sub>+TBAB, H<sub>2</sub>O+CH<sub>4</sub>+TBAB, and H<sub>2</sub>O+N<sub>2</sub>+TBAB.

The CPA parameters of H<sub>2</sub>O and the gases are from the literature [23, 24, 39] and are listed in Table 1.

**Table 1.** CPA parameters of the pure components.

Compound	$b$ [L/mol]	$\Gamma$ [K]	$c_1$	$\epsilon^{A_i B_j} / R$ [K]	$\beta^{A_i B_j}$
H <sub>2</sub> O [24]	0.014515	1017.34	0.6736	2003.25	0.0692
CO <sub>2</sub> [39]	0.0272	1551.222	0.7602	0	0
CH <sub>4</sub> [39]	0.02910	959.028	0.44718	0	0
N <sub>2</sub> [23]	0.02605	634.070	0.49855	0	0

In Table 1,  $b$  is the CPA co-volume parameter (in Eq. (1)),  $\Gamma$  is the CPA reduced energy parameter ( $\Gamma = a_0/(Rb)$ ), and  $c_1$  is the CPA alpha-function temperature-dependence (in Eq. (4)).

In this work, H<sub>2</sub>O is set to a four-site (4C) scheme, and the three gases are set to non-association. The temperature-dependent H<sub>2</sub>O-gas interaction parameters ( $k_{ij}$  in Eq. (3)) are from the literature ( $-0.15508+0.000877T$  [40],  $0.8243-245.33/T$  [40], and  $1.0741-368.3066/T$  [23] for H<sub>2</sub>O-CO<sub>2</sub>, H<sub>2</sub>O-CH<sub>4</sub>, and H<sub>2</sub>O-N<sub>2</sub>, respectively).

Ion size is a critical physical parameter in electrostatic interaction calculations. For the radii of Br<sup>-</sup>, Cl<sup>-</sup> and F<sup>-</sup>, we used the Pauling radii (1.95 Å, 1.81 Å, and 1.36 Å for Br<sup>-</sup>, Cl<sup>-</sup> and F<sup>-</sup>, respectively)

[41]. There are four soft and long hydrophobic alkyl chains on the TBA<sup>+</sup> cation, and the positive charge is sterically hindered by the alkyl substituents [42]. Sun et al. [42] investigated the effects of ion size on thermodynamic modelling performance and gave a value of the TBA<sup>+</sup> radius (2.25 Å), which was chosen in this work.

As discussed above, hydrated ionic radii are used in electrostatic interaction calculations. Because there is no experimental free hydration energy for some ions, to keep the model's universality, the empirical L-P-S equations [43] are used to estimate the hydrated radii:

$$r_{hyd.C} = r_{cation} + 0.85 \text{ \AA} \quad (14)$$

$$r_{hyd.A} = r_{anion} + 0.1 \text{ \AA} \quad (15)$$

In Eqs. (14) and (15),  $r_{cation}$  is the physical radius of TBA<sup>+</sup> (2.25 Å) and  $r_{anion}$  is the Pauling radius of the corresponding anion.  $r_{hyd.C}$  and  $r_{hyd.A}$  are the hydrated ionic radii.

The CPA co-volume parameter of ions can be estimated by [25]:

$$b = 2/3\pi N_A (2r_i)^3 \quad (16)$$

where  $r_i$  is the physical radius ( $r_{cation}$  in Eq. (14) and  $r_{anion}$  in Eq. (15)) of the ion  $i$ .

The  $\epsilon_r$  is critical the electrostatic calculations [44]. By using infrared spectroscopy, Stangret and Gampe [45] found that the number of hydrogen bonds significantly increases in aqueous TBAX solutions. In other words, hydrophobic effects exist in aqueous TBAX solutions. The hydrophobic effects of TBAX can strengthen the hydrogen bonding of water, changing the H<sub>2</sub>O structure around TBA<sup>+</sup>, resulting in an increase of the  $\epsilon_r$  [46].

There are limited experimental values of  $\epsilon_r$  for aqueous TBAX solutions. In modelling research using SAFT-VRE and MPT, the  $\epsilon_r$  of pure solvent has been used in electrostatic interaction calculations. In this work, the  $\epsilon_r$  of pure H<sub>2</sub>O is used in the electrostatic interaction calculations.

In this work, the cation/anion-solvent interaction parameters are evaluated by the regression of MIAC, and the cation/anion-gas interaction parameters are evaluated by the regression of gas solubility in aqueous phase.

The objective function of the regression is:

$$F = \sum_i^{Np} \left[ \frac{x_i^{cal} - x_i^{exp}}{x_i^{exp}} \right]^2 \quad (17)$$

where  $Np$  is the number of experimental data points,  $x_i^{cal}$  represents the calculated values (MIAC of electrolyte and gas solubility), and  $x_i^{exp}$  represents the corresponding experimental values.

The results are presented as the relative average deviation:

$$RAD\% = \frac{1}{Np} \sum_i \left| \frac{y_i^{cal} - y_i^{exp}}{y_i^{exp}} \right| \times 100\% \quad (18)$$

where  $y_i^{cal}$  is the calculated results of a given property (MIAC of electrolyte and gas solubility), and  $y_i^{exp}$  means the corresponding experimental data.

For each H<sub>2</sub>O+TBAX binary system, there is only one adjustable parameter ( $\Delta U_{cation/anion-solvent}$ ). After modeling the H<sub>2</sub>O+TBAX binary system, there is only one adjustable parameter ( $\Delta U_{cation/anion-gas}$ ) for each H<sub>2</sub>O+gas+TBAX system.

## 4. RESULTS AND DISCUSSION

### 4.1 Binary Systems

First, the H<sub>2</sub>O+TBAX systems were modelled. Binary systems containing H<sub>2</sub>O+TBAX, were modelled using CPA in previous works [23, 40]. In this work, the H<sub>2</sub>O+TBAB, H<sub>2</sub>O+TBAC, and H<sub>2</sub>O+TBAF systems are studied.

Table 2 and Figure 1 show the modelling results of the MIAC of TBAX in aqueous solution.

**Table 2.** Cation/anion-H<sub>2</sub>O interaction parameters and modelling performance of the mean ionic activity coefficients of TBAX in aqueous solution.

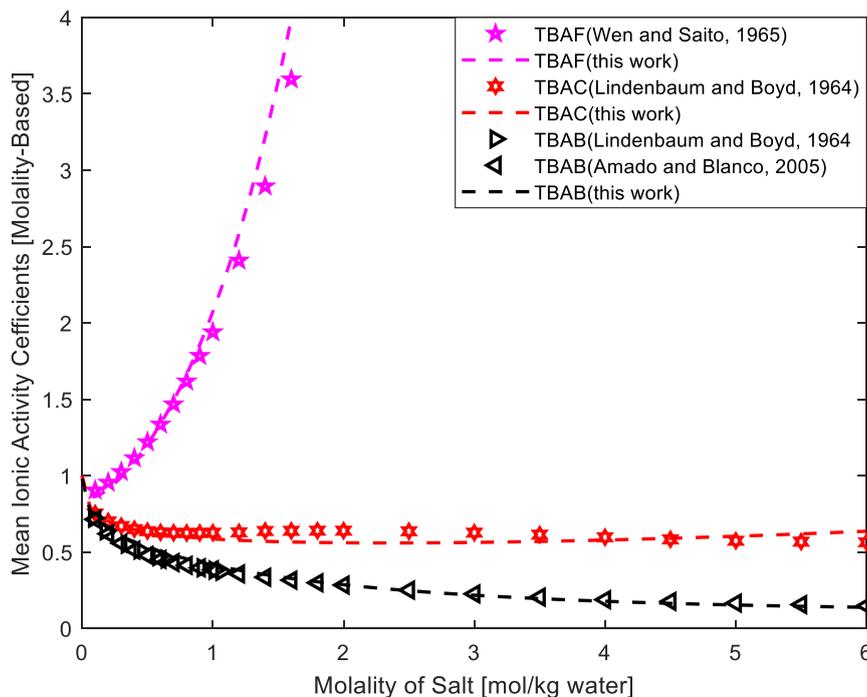
Salt	$\Delta U_{cation/anion-water}$ [J/mol]	m [mol/kg]	RAD $\gamma_{\pm}^m$ [%]
TBAB [47, 48]	-785.1	0.1-6.0	6.3
TBAC [47]	-1318.3	0.1-6.0	6.0
TBAF [49]	-2167.7	0.1-1.6	4.9

In Table 2,  $\Delta U_{cation/anion-water}$  is cation/anion-H<sub>2</sub>O interaction parameters (from Eq. (13)), m is molality, and  $\gamma_{\pm}^m$  is MIAC of TBAX.

From Table 2, it can be observed that our model overall correlates well the MIAC of TBAX in aqueous solution at reference temperature (298.15 K). Compared with the performance of other models, the performance of this work is worse than that of those using SAFT-VRE and similar to that of those using e-CPA. SAFT-VRE uses different cation radii for each electrolyte; additionally, in one SAFT-VRE modelling work [17], there were three interaction parameters for a single-electrolyte/single-H<sub>2</sub>O system at reference temperature and another temperature-dependent parameter for wide temperature ranges. In Ma et al.'s work [22], there were four adjustable parameters for a single-electrolyte/single-H<sub>2</sub>O system at reference temperature and no temperature-dependent parameter. Unfortunately, the reports using MPT did not give details of the modelling performance. In a e-CPA modelling work [42], there was only one adjustable parameter for a single-electrolyte/single-H<sub>2</sub>O system at reference temperature and two extra temperature-dependent parameters for wide temperature ranges. In this work, there is only one interaction parameter, and temperature dependence is not considered.

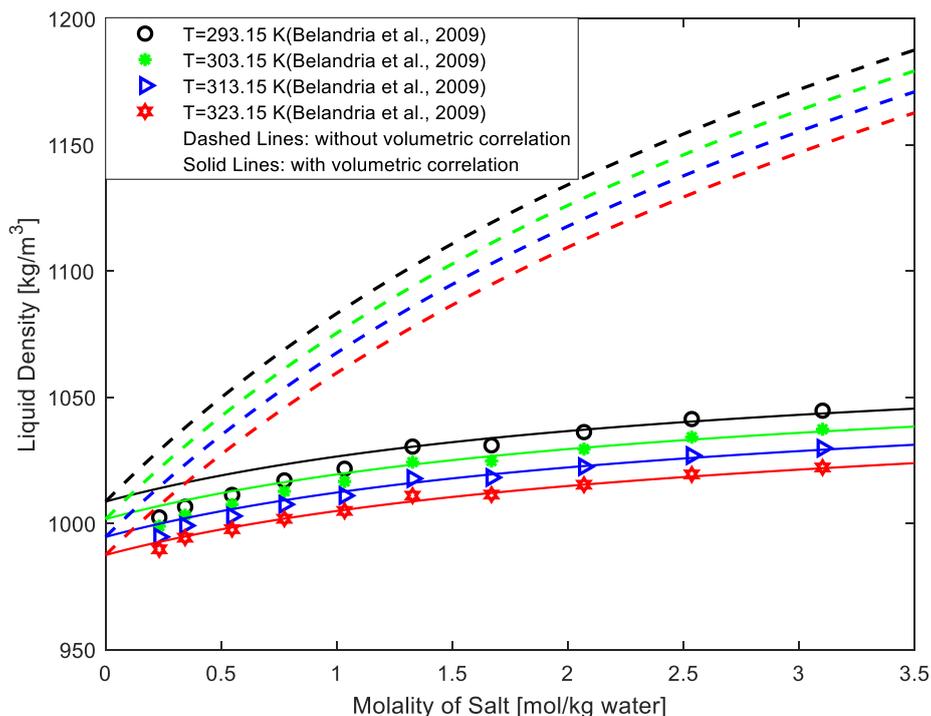
It can be seen from Figure 1 that for a given electrolyte molality, the order of the values of MIAC are: TBAB<TBAC<TBAF. It is also observed that the absolute value of the interaction parameter between the cation/anion and H<sub>2</sub>O is inversely proportional to ion radii of halides. This phenomenon may be explained in that smaller ion radii of halides cause large ions-H<sub>2</sub>O interactions.

The experimental data of MIAC show the complex relationship of electrolyte molality. For the H<sub>2</sub>O+TBAB system, the values decrease with increasing TBAB molality (at low to medium TBAB molality). For the H<sub>2</sub>O+TBAC system, at low TBAC molality, the values of MIAC first decrease and then increase with increasing molality. After reaching maximum values, the MIAC of TBAC next decrease and then increase slightly. The values of the MIAC of TBAF in aqueous solution increase sharply with increasing TBAF molality. Wen and co-workers [49] explained that this phenomenon of TBAF could be attributed to the smaller radius of F<sup>-</sup>, which may tend to immobilize H<sub>2</sub>O around it due to its high charge density [49].



**Figure 1.** Mean ionic activity coefficients of TBAX in aqueous solution [47-49] at 298.15 K.

TBA<sup>+</sup> is large and hydrophobic; its size and hydrophobic effects help TBA<sup>+</sup> strengthen the “cage-like” H<sub>2</sub>O structure [45]. The hydrophobic properties could be why the MIAC of TBAX shows an unexpected trend similar to that of common inorganic salts (e.g., NaCl).



**Figure 2.** Densities of aqueous TBAB solutions [50] at different salt molalities and temperatures.

Liquid density is a critical property in industrial applications. Until now, only experimental densities of aqueous TBAB solution have been reported (with a narrow molality range) [50].

The modelling results shown in Figure 2 (dashed lines) show that this work overestimates the liquid densities of aqueous TBAB solution. In fact, other models also overestimate the liquid density of aqueous TBAB solution. In aqueous TBAX solutions,  $TBA^+$  is large and has hydrophobic effects, so the existence of  $TBA^+$  results in the formation of ice-like structures (with low density) of  $H_2O$  molecules around  $TBA^+$  [17]. Both our model and prior models consider TBAX to be completely dissociated into ions in  $H_2O$ , and the hydrophobic effects are not included. Thus, these models may not be able to accurately represent this special phenomenon.

Here, we try to perform a volumetric correction of liquid densities. Since the deviations may come from the hydrophobic effects of  $TBA^+$ , we set a correlation parameter  $HV_{TBA}$  to improve the prediction ability of liquid densities:

$$v = v^{e-EoS} + x_{TBA}HV_{TBA} \quad (19)$$

where  $v^{e-EoS}$  is the calculated molar volume without correlation,  $x_{TBA}$  is the mole fraction of  $TBA^+$ ,  $HV_{TBA}$  is the volumetric correction coefficient of  $TBA^+$ , and  $v$  is the molar volume of aqueous TBAX solutions. The volumetric correlation results (solid lines in Figure 2) show satisfactory agreement with experimental data (with RAD=0.6%). However, we can also see from Figure 2 that the correlation parameter does perform well for liquid densities at low TBAB molality and low temperature.

#### 4.2 Ternary Systems

Hydrates have potential applications in gas sequestration and gas transportation [6].  $CO_2$  and  $N_2$  are the main components of flue gas, and  $CO_2$  can also be used as a displacement medium for  $CH_4$  hydrate production [6]. Investigations of  $H_2O$ +gas (i.e.,  $CO_2$ ,  $CH_4$ , and  $N_2$ )+TBAX ternary systems are necessary for TBAX hydrate modelling.

Only experimental data of  $H_2O$ +gas+TBAB systems are available. Though experimental data for  $H_2O$ +gas+TBAB are few, the accuracy of some datasets are doubtful. Here, we used the experimental data of  $H_2O$ +gas+TBAX systems that were selected in the previous work [23].

Before presenting the modelling results, it is necessary to review some related definitions and mechanisms. The gas solubility in liquid is defined as the maximum limit of gas that can be dissolved at a specified condition [51]. Gas solubility is easy to measure compared to the vapour phase, so most studies present gas solubility as vapour–liquid–equilibria data.  $CO_2$ ,  $CH_4$ , and  $N_2$  are not very soluble in  $H_2O$ . The two widely accepted mechanisms of gas dissolution are (1) the vacancy mechanism [52] (i.e., the gas filling of  $H_2O$  molecule interstices [52, 53]) and (2) the solvation mechanism [52] (i.e., the ion substitution for  $H_2O$  molecules in the structural framework of  $H_2O$  [52, 53]). The definitions of salting-in effects and salting-out effects are the increase and decrease of gas solubility due to the presence of electrolyte, respectively.

Table 3 and Figures 3 through 5 show the modelling results of gas solubility in aqueous TBAB solutions.

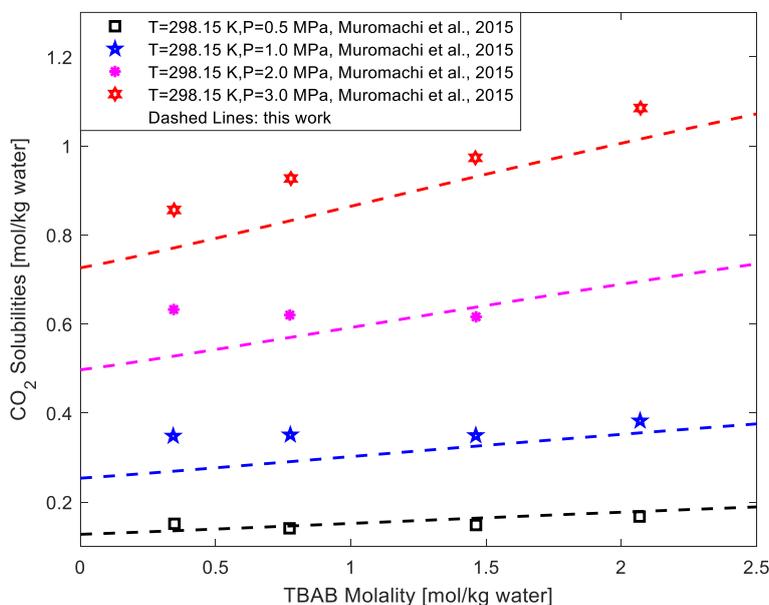
**Table 3.** Cation/anion-gas interaction parameters and modelling performance of gas solubility in aqueous TBAB solutions.

Gas	T [K]	P [MPa]	m [mol/kg]	$\Delta U_{cation/anion-gas}$ [J/mol]	RAD $x_{gas}$ [%]
CO <sub>2</sub> [54, 55]	286.15-303.1	0.2-4.0	0.342-2.074	3920.2	7.4
CH <sub>4</sub> [56, 57]	278.15-308.15	0.101	0.096-4.01	4795.4	5.4
N <sub>2</sub> [58]	283.15-298.15	0.101	0-1.0	4987.6	2.9

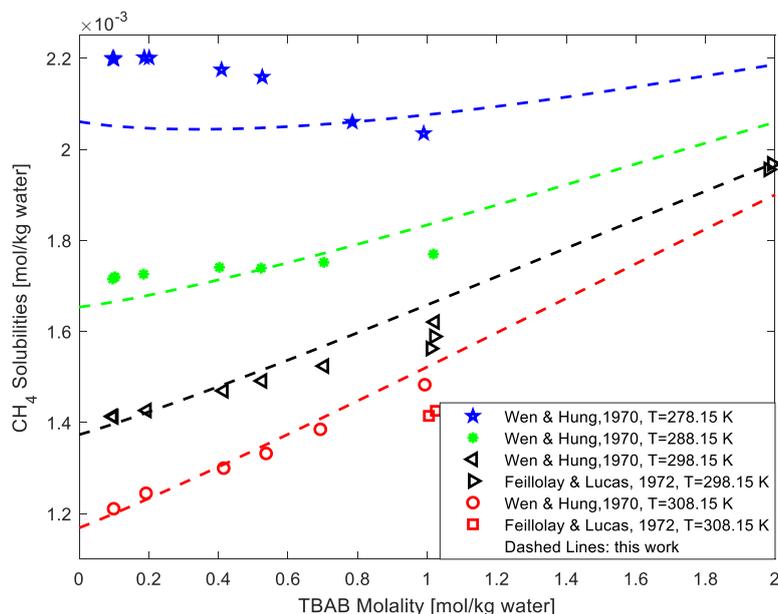
In Table 3,  $\Delta U_{cation/anion-gas}$  is the cation/anion-gas interaction parameters (from Eq. (13)), T is the temperature range, P is the pressure range, m is the molality range, and  $x_{gas}$  is gas solubility.

From Table 3, it can be observed that our model correlates well the gas solubility in aqueous TBAB solutions over wide electrolyte molality ranges, especially for N<sub>2</sub>. The deviations for CO<sub>2</sub> are larger, with RAD greater than 7%. This result may be due to the deviations among the different experimental datasets [54, 55]. Among the published e-EoS modelling works, only a e-CPA modelling contribution [23] gave the performance details. The performance of our model is better than that of e-CPA. The difference in performance may mainly come from the different values of MIAC. e-CPA has two temperature-dependent adjustable parameters, but for these narrow temperature ranges, it seems that the temperature dependence of  $\Delta U_{cation/anion-gas}$  can be ignored.

The solubility of gases in pure H<sub>2</sub>O follow the sequence of  $x_{CO_2} > x_{CH_4} > x_{N_2}$  at the same pressure and temperature [40]. It can be observed from Table 3 that the absolute values of  $\Delta U_{cation/anion-gas}$  show the reverse order ( $\Delta U_{cation/anion-CO_2} < \Delta U_{cation/anion-CH_4} < \Delta U_{cation/anion-N_2}$ ).



**Figure 3.** CO<sub>2</sub> solubility in aqueous TBAB solutions [55] at 298.15 K and different pressures.

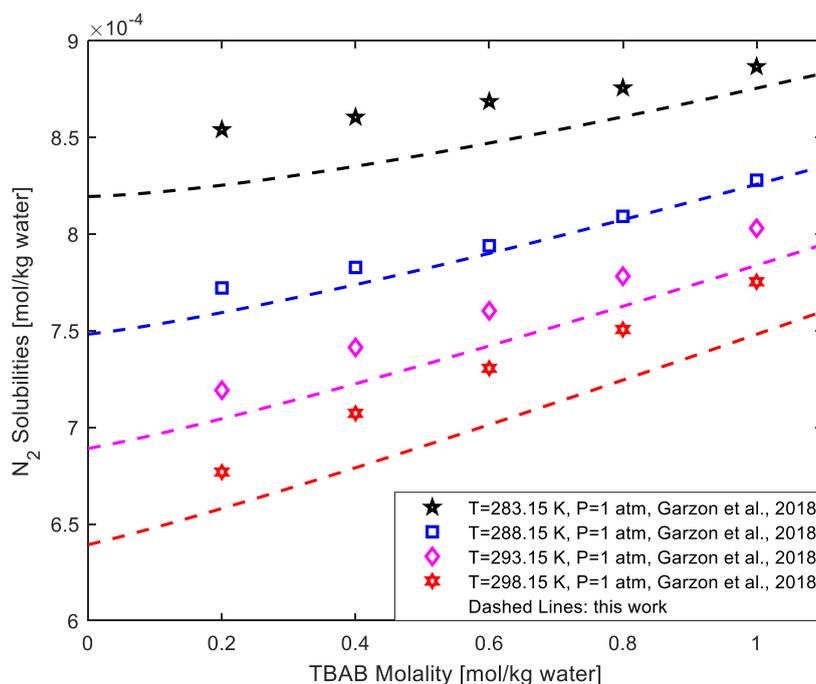


**Figure 4.** CH<sub>4</sub> solubility in aqueous TBAB solutions [56, 57] at atmospheric pressure and different temperatures.

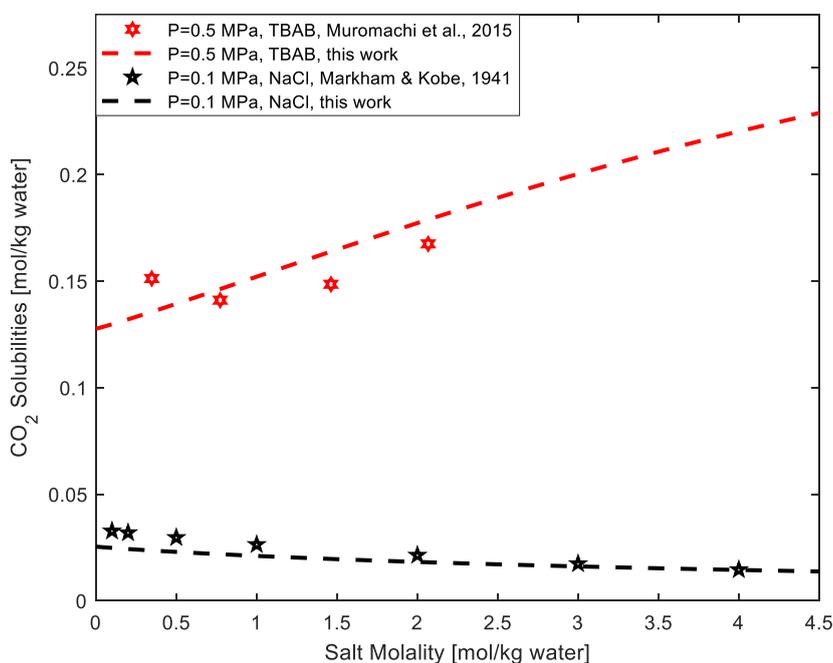
Among H<sub>2</sub>O+gas+TBAX systems, H<sub>2</sub>O+CO<sub>2</sub>+TBAB is the most studied. It can be observed from Figure 3 that our model correlates well with the CO<sub>2</sub> solubility in aqueous TBAB solutions. From Figure 3, we can also observe that the salting effects of TBAB on CO<sub>2</sub> solubility are complex. At different molalities and pressures, TBAB has different salting effects on CO<sub>2</sub>. Lin and co-workers [54] stated that the salting effects of TBAB on CO<sub>2</sub> are different at different temperatures, pressures, and molalities. For the H<sub>2</sub>O+CO<sub>2</sub>+TBAB system, Lin and co-workers [54] noted that there is no clear region for salting-in or salting-out effects.

Unfortunately, some researchers [17, 20] did not consider the salting effects of TBAB on CO<sub>2</sub> solubility, i.e., they took the CO<sub>2</sub> solubility in aqueous TBAB solutions to be equal to that in pure H<sub>2</sub>O at the same temperature and pressure [17].

From Figure 4, we can see that TBAB has complex salting effects on CH<sub>4</sub> solubility. TBAB has slight salting-out effects on CH<sub>4</sub> at lower temperatures (e.g., 278.15 K) but has significant salting-in effects on CH<sub>4</sub> at higher temperatures (e.g., 308.15 K). With increasing temperature, the salting-in effects become increasingly significant.



**Figure 5.** N<sub>2</sub> solubility in aqueous TBAB solutions [58] at atmospheric pressure and different temperatures.



**Figure 6.** CO<sub>2</sub> solubility in aqueous solutions [55, 59] at 298.15 K and different pressures.

It can be seen from Figure 5 that TBAB has significant salting-in effects on N<sub>2</sub> solubility in H<sub>2</sub>O, and the salting-in effects are more significant at higher temperatures (e.g., 298.15 K). Based on experimental data, Garzon et al. [58] noted that N<sub>2</sub> solubility increases as molality increases in a specific temperature-pressure-molality range (with molality=0.2-1.0 mol/kg, temperatures=283.15-298.15 K, and pressure=101.325 kPa).

TBAB has different salting effects on different gases in H<sub>2</sub>O at low temperatures, i.e., salting-out effects on CH<sub>4</sub> and salting-in effects on N<sub>2</sub>.

Figure 6 shows the comparison of CO<sub>2</sub> solubility in aqueous solutions of NaCl [59] and TBAB [55]. It can be clearly seen from Figure 6 that NaCl has significant salting-out effects on CO<sub>2</sub> solubility, while TBAB has significant salting-in effects on CO<sub>2</sub> solubility. Based on the mechanisms of gas dissolution mentioned above, the main reason for the salting-out effects of inorganic salts on gas solubility in H<sub>2</sub>O is the formation of ion solvation, which reduces the number of interstices of H<sub>2</sub>O and results in the escape of gas molecules from solution [60]. However, TBAB instead causes the salting-in of hydrophobic solutes under specific conditions, and some explanations for this effect [54, 56, 61] have been proposed. The acceptable explanations are as follows. (1) Anions (i.e., Br<sup>-</sup>, Cl<sup>-</sup> and F<sup>-</sup>) and cations (TBA<sup>+</sup>) form ion hydrations [56], which result in the salting-out effect of TBA<sup>+</sup> on gas, and this salting-out effect weakens with increasing temperature. (2) A “disorganization effect” [61] caused by the hydrophobic effect of TBA<sup>+</sup>; this “disorganization effect” results in the salting-in effect, and this salting-in effect strengthens as the temperature and TBAX molality increase. The combination of these two opposite effects yields the salting effects of TBAB on gas solubility.

TBAB has significant salting effects on gas solubility, but many modelling works ignore the salting effects of TBAB [11, 17, 20] or consider the salting effects of TBAB to be relatively small [13]. None of the e-EoS modelling works (i.e., SAFT-VRE [17], MPT [22], and e-CPA [23]) and our model do consider the hydrophobic effects of TBAB. Consequently, these models may not be able to accurately represent the “disorganization effect”.

## 5. CONCLUSIONS

The salting effects of tetra-*n*-butyl ammonium halides on gas solubility in H<sub>2</sub>O are complex at different temperatures and electrolyte molalities, and almost no explicit region of salting-in or salting-out effects is observed. The salting-in effects of tetra-*n*-butyl ammonium halides on gas solubility in H<sub>2</sub>O tend to appear at relatively high temperatures and pressures. The hydrophobic effect of the tetra-*n*-butyl ammonium cation plays a significant role in phase behaviours.

This work presents a novel electrolyte model by extending the Cubic Plus Association Equation of State. This novel model applies Debye-Hückel theory to perform electrostatic interaction calculations. In the electrostatic interaction calculations, hydrated ionic radii are used to take ion-water interactions into account. Then, a modelling study for aqueous tetra-*n*-butyl ammonium halide solutions is presented.

The cation/anion-water interaction parameters are evaluated from the regression of the experimental mean ionic activity coefficients (MIAC) of tetra-*n*-butyl ammonium halide in aqueous solution, and the cation/anion-gas interaction parameters are evaluated from the regression of experimental gas solubility in aqueous solution. The results show that this model can correlate the MIAC of tetra-*n*-butyl ammonium halides reasonably well in aqueous solutions over wide electrolyte molality ranges. The model overestimates liquid densities.

This model considers tetra-n-butyl ammonium halides as strong electrolytes and does not take the hydrophobic effects of salts into account. Adding chemical equilibrium to this model is a potential enhancement for tetra-n-butyl ammonium halide systems in which hydrophobic effects exist.

#### ACKNOWLEDGEMENTS

The authors thank College of Mechanical and Electrical Engineering in Hohai University, Department of Chemical and Biochemical Engineering in Technical University of Denmark, and School of Energy and Power Engineering in Wuhan University of Technology for supporting this research.

#### References

1. G.A. Jeffrey, *Accounts of Chemical Research*, 2 (1969) 344.
2. R. McMullan, G.A. Jeffrey, *The Journal of chemical physics*, 31 (1959) 1231.
3. S.S. Fan, S.F. Li, J.Q. Wang, X.M. Lang, Y.H. Wang, *Energy & Fuels*, 23 (2009) 4202.
4. J. Deschamps, D. Dalmazzone, *Journal of thermal analysis and calorimetry*, 98 (2009) 113.
5. L.L. Shi, D.Q. Liang, *Fluid Phase Equilibria*, 386 (2015) 149.
6. J.E.D. Sloan, C.A. Koh, C. Koh, *Clathrate hydrates of natural gases*, CRC press, 1 (2007) 9.
7. D.L. Fowler, W.V. Loebenstein, D.B. Pall, C.A. Kraus, *Journal of the American Chemical Society*, 62 (1940) 1140.
8. C.C. Chen, H. Britt, J.F. Boston, L.B. Evans, *AIChE Journal*, 28 (1982) 588.
9. J.M. Herri, A. Bouchemoua-Benaissa, M. Kwaterski, A. Fezoua, Y. Ouabbas, A. Cameir~ao, *Fluid Phase Equilibria*, 301 (2011) 171.
10. G. Soave, *Chemical engineering science*, 27 (1972) 1197.
11. J. Verrett, J.S. Renault-Crispo, P. Servio, *Fluid Phase Equilibria*, 388 (2015) 160.
12. M.A. Trebble, P.R. Bishnoi, *Fluid Phase Equilibria*, 35 (1987) 1.
13. A. Eslamimanesh, A.H. Mohammadi, D. Richon, *Chemical engineering science*, 81 (2012) 319.
14. D.Y. Peng, D.B. Robinson, *Industrial & Engineering Chemistry Fundamentals*, 15 (1976) 59.
15. H. Najibi, K. Momeni, M.T. Sadeghi, A.H. Mohammadi, *The Journal of Chemical Thermodynamics*, 87 (2015) 122.
16. J.P. Simonin, S. Krebs, W. Kunz, *Industrial & Engineering Chemistry Research*, 45 (2006) 4345.
17. P. Paricaud, *The Journal of Physical Chemistry B*, 115 (2011) 288.
18. Y.Y. Zuo, T.M. Guo, *Chemical engineering science*, 46 (1991) 3251.
19. B. Maribo-Mogensen, K. Thomsen, G.M. Kontogeorgis, *AIChE Journal*, 61 (2015) 2933.
20. A. Fukumoto, P. Paricaud, D. Dalmazzone, W. Bouchafaa, T.T.S. Ho, W. Fürst, *Journal of chemical & engineering data*, 59 (2014) 3193.
21. P. Babu, P. Paricaud, P. Linga, *Fluid Phase Equilibria*, 413 (2016) 80.
22. Q.L. Ma, J.L. Qi, G.J. Chen, C.Y. Sun, *Fluid Phase Equilibria*, 430 (2016) 178.
23. L. Sun, X.D. Liang, N.V. Solms, G.M. Kontogeorgis, *Fluid Phase Equilibria*, 507 (2020) 112423.
24. G.M. Kontogeorgis, E.C. Voutsas, I.V. Yakoumis, D.P. Tassios, *Industrial & Engineering Chemistry Research*, 35 (1996) 4310.
25. G.M. Kontogeorgis, G.K. Folas, *Thermodynamic models for industrial applications: from classical and advanced mixing rules to association theories*, John Wiley & Sons, 15 (2009) 463.
26. D.C. Rapaport, *Molecular Physics*, 50 (1983) 1151.
27. M.L. Michelsen, E.M. Hendriks, *Fluid Phase Equilibria*, 180 (2001) 165.
28. M. Valiskó, D. Boda, *The Journal of Physical Chemistry B*, 119 (2015) 1546.
29. M. Valiskó, D. Boda, *Molecular Physics*, 115 (2017) 1245.
30. L. Sun, X.D. Liang, N.V. Solms, G.M. Kontogeorgis, *Industrial & Engineering Chemistry Research*, 59 (2020) 11790.

31. A.H. Harvey, J.M. Prausnitz, *AIChE Journal*, 35 (1989) 635.
32. K. Aasberg-Petersen, E. Stenby, A. Fredenslund, *Industrial & Engineering Chemistry Research*, 30 (1991) 2180.
33. R. Sun, J. Dubessy, *Geochimica et Cosmochimica Acta*, 88 (2012) 130.
34. P. Debye, E. Hückel, *Physikalische Zeitschrift*, 24 (1923) 185.
35. J.L. Lebowitz, J.K. Percus, *Physical Review*, 144 (1966) 251.
36. B. Maribo-Mogensen, G.M. Kontogeorgis, K. Thomsen, *Industrial & Engineering Chemistry Research*, 51 (2012) 5353.
37. M. Born, *Zeitschrift für Physik*, 1 (1920) 45.
38. D. Fraenkel, *The Journal of Physical Chemistry B*, 116 (2012) 3603.
39. I. Tsvintzelis, G.M. Kontogeorgis, M.L. Michelsen, E.H. Stenby, *Fluid Phase Equilibria*, 306 (2011) 38.
40. L. Sun, G.M. Kontogeorgis, N.V. Solms, X.D. Liang, *Industrial & Engineering Chemistry Research*, 58 (2019) 17555.
41. L. Pauling, *The Nature of the Chemical Bond*, Cornell university press Ithaca, 5 (1960) 260.
42. L. Sun, X.D. Liang, N.V. Solms, G.M. Kontogeorgis, *Fluid Phase Equilibria*, 486 (2019) 37.
43. W.M. Latimer, K.S. Pitzer, C.M. Slansky, *Journal of Chemical Physics*, 7 (1993) 108.
44. J.L. Burgot, *The notion of activity in chemistry*, Springer International Publishing, 5 (2017) 35.
45. J. Stangret, T. Gampe, *The Journal of Physical Chemistry B*, 103 (1999) 3778.
46. R.W. Gurney, *Ionic processes in solution*, McGraw-Hill, 2 (1953) 54.
47. S. Lindenbaum, G.E. Boyd, *The Journal of Physical Chemistry*, 68 (1964) 911.
48. E. Amado, L.H. Blanco, *Fluid Phase Equilibria*, 233 (2005) 230.
49. W.Y. Wen, S.J. Saito, C.M. Lee, *The Journal of Physical Chemistry*, 70 (1966) 1244.
50. V. Belandria, A.H. Mohammadi, D. Richon, *The Journal of Chemical Thermodynamics*, 41 (2009) 1382.
51. M. Silberberg, *Principles of general chemistry*, McGraw-Hill, 3 (2012) 71.
52. A.F. Borina, O.Y. Samojlov, *Zhurnal Strukturnoj Khimii*, 15 (1974) 395.
53. M.S. Jhon, H. Eyring, Y.K. Sung, *Chemical Physics Letters*, 13 (1972) 36.
54. W. Lin, D. Dalmazzone, W. Fürst, A. Delahaye, L. Fournaison, P. Clain, *Journal of chemical & engineering data*, 58 (2013) 2233.
55. S. Muromachi, A. Shijima, H. Miyamoto, R. Ohmura, *The Journal of Chemical Thermodynamics*, 85 (2015) 94.
56. W.Y. Wen, J.H. Hung, *The Journal of Physical Chemistry*, 74 (1970) 170.
57. A. Feillolay, M. Lucas, *The Journal of Physical Chemistry*, 76 (1972) 3068.
58. L.C.A. Garzon, A.F. Suarez, C.M. Romero, *The Journal of Chemical Thermodynamics*, 126 (2018) 105.
59. A.E. Markham, K.A. Kobe, *Journal of the American Chemical Society*, 63 (1941) 449.
60. P.J. Carvalho, L.M.C Pereira, N.P.F. Gonçalves, A.J. Queimada, J.A.P. Coutinho, *Fluid Phase Equilibria*, 388 (2015) 100.
61. B. Hribar-Lee, K.A. Dill, V. Vlachy, *The Journal of Physical Chemistry B*, 114 (2010) 15085.